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⑭ 発明の名称 ポリテトラフロロエチレン系繊維

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## 明 細 書

## 1. 発明の名称

ポリテトラフロロエチレン系繊維

## 2. 特許請求の範囲

(1) 平均繊維度が3.0d以下であるポリテトラフロロエチレン系重合体からなる焼結体繊維であって、かつ小角X線散乱法により $2\theta = 1^\circ$ の小角X線散乱強度を測定した時の値が80cps以下であることを特徴とするポリテトラフロロエチレン系繊維。

(2) 前記 $2\theta = 1^\circ$ での小角X線散乱強度が50cps以下であるポリテトラフロロエチレン系繊維。

## 3. 発明の詳細な説明

〔産業上の利用分野〕

本発明は、3.0d以下という極細のポリテトラフロロエチレン系繊維に関するものである。

〔従来の技術〕

ポリテトラフロロエチレン(以下単にPTFEという)系繊維は産業用素材を始めとして広範囲

の分野に、その離型性などの特性のために重宝されている。

従来、PTFE系重合体は、重合体溶液粘度が高くノズル詰りが惹起し易く、また曳糸性も悪くて製糸切れし易い欠点があり、現在のところ精々5dが最も細い繊維のものとして存在するにすぎず、これ以上に細い繊維は製造生産が困難と見做されており、産業的に製品化されていないのが実情である。

〔発明が解決しようとする問題点〕

本発明は、かかるPTFE系繊維の極細化について検討した結果、極細繊維でありながら強力に優れ、単糸切れや毛羽立ちがなく、摩擦係数が極めて小さく、寸法安定性のよいPTFE繊維を提供し得たものである。

本発明により、従来からの重くて取扱いにくい繊維というイメージの強いPTFE系繊維の概念を根本的に打破し、これまで用途展開できなかった分野にも十分に適用可能であり、さらに極細であるから他種繊維や他種樹脂との混用や分散が容

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POLYTETRAFLUOROETHYLENE FIBER  
[Poritetorafuroroechiren kei sen'i]

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1. Title of the Invention

Polytetrafluoroethylene Fiber

2. Claims

(1) <sup>c</sup>Polytetrafluoroethylene fiber characterized by being sintered fiber having the average fineness of no more than 3.0d and composed of a polytetrafluoroethylene polymer and by the small angle X-ray scattering intensity measured at  $2\theta = 1^\circ$  by small angle X-ray scattering being no more than 80cps.

(2) Polytetrafluoroethylene fiber characterized by the above-mentioned small angle X-ray scattering intensity measured at  $2\theta = 1^\circ$  being no more than 50cps.

3. Detailed Description of the Invention

[Field of Industrial Application]

The present invention relates to polytetrafluoroethylene fibers that are no more than 3.0d and extremely fine.

[Related Art of the Invention]

Polytetrafluoroethylene (henceforth, simply PTFE) fibers are favorably utilized in a wide range of fields including industrial materials because of their mold-releasing properties and the like.

Conventional PTFE polymers have disadvantages in that they are susceptible to clogging nozzles due to their high viscosities as polymer solutions and also in that they are likely to break during the manufacture of yarns due to their poor thread-forming properties. Currently, the finest

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\* Numbers in the margin indicate pagination in the foreign text.

fibers have the fineness of 5d at the smallest, and any finer fibers are considered difficult to manufacture and are therefore not being industrially commercialized.

[Problems that the Invention is to Solve]

As a result of studying the methods for achieving ultra-fineness for such PTFE fibers, the invention provides PTFE fibers that have excellent strength while being ultrafine, that are free of single-thread breakage or fuzzing, and that have extremely small frictional coefficients and dimensional stability.

By fundamentally breaking down the conventional concept of PTFE fibers of being heavy and difficult to handle, the invention allows for their applications in fields in which they could not be utilized in the past and demonstrates how easily they can be blended or dispersed with other types of fibers or other types of resins because of their ultra-fineness. /100

By utilizing the above characteristics, it is also possible to fully demonstrate their properties in quantities much smaller than in the past, and the flexibility of the PTFE fibers in terms of application planning can be increased significantly.

[Means for Solving the Problems]

The invention has the following structure.

(1) Polytetrafluoroethylene fiber characterized by being sintered fiber having the average fineness of no more than 3.0d and composed of a polytetrafluoroethylene polymer and by the small angle X-ray scattering intensity measured at  $2\theta = 1^\circ$  by small angle X-ray scattering being no

more than 80cps.

(2) Polytetrafluoroethylene fiber characterized by the above-mentioned small angle X-ray scattering intensity measured at  $2\theta = 1^\circ$  being no more than 50cps.

In this invention, a PTFE polymer indicates a homopolymer of tetrafluoroethylene or a copolymer composed of tetrafluoroethylene at no less than 90 mol%, preferably 95 mol% or higher, of the whole.

Examples of monomers copolymerizable with tetrafluoroethylene are, but not limited to: vinyl fluoride compounds such as trifluoroethylene, trifluorochloroethylene, tetrafluoropropylene, hexafluoropropylene, etc.; and vinyl compounds such as propylene, ethylene, isobutylene, styrene, acrylonitrile, etc.

From among the above monomers, vinyl fluoride compounds, particularly ones containing large quantities of fluoride, are preferred from the perspective of fiber properties.

The PTFE fiber mentioned in the invention is fiber that has the average fineness of no more than 3.0d, preferably 2.0d or less, although its effects become increased as it becomes finer, and its fineness should even more preferably be 1.0d or less.

PTFE fiber of the invention has the characteristic in that its small angle X-ray scattering intensity measured at  $2\theta = 1^\circ$  by small angle X-ray scattering is 80cps, preferably 50cps or less, and more preferably 40cps or less.

If it exceeds 80cps, the fiber becomes brittle and the flexibility in application planning diminishes in terms of the fiber properties. In

other words, PTFE fiber of the invention is dense with the density of the microvoids of the constituent polymer crystals being low.

In addition to the small angle X-ray scattering intensity being low as mentioned in the above, fiber of the invention is also characterized by the fact that the crystal size of (110) crystal face measured by wide angle X-ray diffraction (counter method) is no less than  $95\text{\AA}$ , preferably  $100\text{\AA}$  or greater. Large crystal sizes indicate that the crystals have grown that much thicker.

Because of the synergistic effect of the small angle X-ray scattering intensity and the crystal sizes at the (110) crystal face mentioned in the above, PTFE fiber of the invention, despite being ultrafine, contains crystals that have sufficiently grown and therefore has excellent strength and dimensional stability.

The small angle X-ray scattering intensity is measured as follows.

A fiber specimen is arranged in the fiber axial direction and cut out in the lengths of 4cm. 60mg of the specimen was weighed and charged in a die 1mm in depth and 2mm in width, solidified by using a collodion solution, and a rectangular cylinder is obtained as a result to be used as a sample.

The sample is then placed perpendicular to an X-ray beam, and the scattering intensity of  $2\theta = 1^\circ$  scanned at the small direction angle of between  $0$  and  $3^\circ$  is measured under the following conditions.

Measuring method: small angle X-ray scattering (small angle X-ray diffraction)

X-ray generator: RU-200B by Rigaku Industrial Corp. (rotating anode type)

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X-ray source: CuK $\alpha$  (a flat graphite single-crystal incident monochromater used)

Output: 40kV, 200mA

Optical system: Kurakkii [as transliterated] camera made by Rigaku Industrial Corp.

U slit: width = 70 $\mu$ m, height = 10mm

Light-receiving side:

light receiving slit = 0.14mm  
longitudinal limit slit = 15mm  
scatter preventing slit = 0.3mm  
longitudinal scatter preventing slit = 6mm

Detector: scintillation counter

The data obtained from this counter is fed to a tally device, which will then make a chart.

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The crystal sizes of the (110) crystal surface mentioned in the invention are measured as follows.

A fiber specimen is arranged in the fiber axial direction and cut out in the lengths of 4cm. 20mg of the specimen is weighed and charged in a die 1mm in depth and 1mm in width, solidified by using a collodion solution, and a rectangular cylinder is obtained as a result to be used as a sample.

The obtained sample is then placed perpendicular to an X-ray beam. Scanning is carried out between 0 and 90° of the angle of direction by a transmission method. Based on the entire width (half-value width) B and the directional angle, 2 $\theta$ , of the location 1/2 of the maximum of the intensity distribution of the peak band (in the vicinity of about 18.3°) of the (110) crystal surface, the following calculation is carried out



based on the Scherrer equation.

$$L = K\lambda / [(B-b) \cdot \cos\theta]$$

wherein K is 1.0, b is 0.0105rad, and  $\lambda$  is 1.5418Å.

The peak band of the (110) crystal surface is measured by the following method.

Measuring method: wide angle X-ray diffraction (counter method)

X-ray generator: RU-200B by Rigaku Industrial Corp. (rotating anode type)

X-ray source: CuK $\alpha$  (a Ni filter used)

Output: 35kV, 15mA

Goniometer: goniometer made by Rigaku Industrial Corp.

Slit system: 2mm $\Phi$ , 1° - 1°

Detector: scintillation counter

The data obtained from this counter is fed to a tally device, which will then make a chart.

PTFE fiber of the invention has the following fiber properties.

It has balanced properties of strength of 1.0g/d or greater, preferably 1.5g/d or greater, elongation of 30% or less, preferably 20% or less, and dry-heat contraction percentage (230°C  $\times$  30) of 20% or less, preferably 15% or less. In particular, the elongation is drastically different from that of conventional PTFE fiber which was around 40%.

Despite being ultrafine (no more than 3.0d), the PTFE fiber of the invention has the above-mentioned balanced fiber properties with excellent dimensional stability. Therefore, it is highly compatible with various types of fibers and various types of resins and can be readily blended

or dispersed with them evenly and easily. Also, modification of its surface properties can be accomplished with a smaller quantity because of its fineness.

One example of the method for producing PTFE fiber of the invention will be described below. % mentioned hereafter in the invention indicates % by weight.

As a characteristic of the production technique of the invention, it can be mentioned that the fiber-forming concentrate solution as well as all of the water and chemical agents utilized in the individual processes including rinsing and alkali treatment are systems that are highly pure and contain only small amounts of impurities (foreign matters). By using these systems, it is possible for the first time to provide fiber for which single-thread breakage and fuzzing are controlled and which contain sufficiently grown crystals and only a few voids. Moreover, the particles generated during the processes should be controlled as much as possible, and large foreign matters should be removed.

As the fiber-forming concentrate solution of the invention, a mixed solution of a viscose and a PTFE emulsion is discharged into a coagulation bath to be solidified and is then rinsed with water to be refined. After the refinement, it is immersed in alkaline water and then squeezed. It is then either dried first or directly led to a calcination process without being dried, in which it is calcined and drawn. The calcination and drawing may be carried out separately. Next, this calcined fiber is matured by means of oxidation in a high-temperature atmosphere.

The water used in each process of the invention is either

ion-exchanged water or distilled water.

The PTFE emulsion consists of ion-exchanged water containing 20 - 75%, preferably around 60%, of PTFE blended and dispersed in it. Although a nonionic surfactant or anionic surfactant can be utilized as a dispersant, a nonionic surfactant is specified in this case. The combined amount is between 3 and 10% with respect to the amount of PTFE. Examples of such dispersant include a polyoxyalkylene glycol-type nonionic surfactant and alkylaryl polyether alcohol (TRITON X-100).

The sizes of the emulsion are between about 0.005 and  $1\mu$ , although smaller sizes result in better fiber-forming properties and fiber properties. Preferably, the average grain size should be adjusted to no more than  $0.6\mu$ .

The viscose is a composition containing between 3 and 15%, preferably between 5 and 10%, of cellulose, between 2 and 12%, preferably /102 between 6 and 9% of caustic soda, and between 27 and 32%, preferably between 28% and 30% of carbon disulfide, and the degree of its polymerization is between 200 and 600, preferably between 300 and 400. The higher the degree of maturation (aging) of the composition, the better.

The above PTFE emulsion and viscose are mixed together to prepare a fiber-forming concentrate solution. At this time, the composition is adjusted so that the PTFE contained inside the mixture polymer of the fiber-forming concentrate solution is between 60 and 90%, preferably between 70 and 96%, more preferably between 87 and 93%. The higher the PTFE concentration, the better the fiber properties will be. In other words, the cellulose concentration in the fiber-forming concentrate

solution is between 5 and 20%, preferably between about 10 and 15%.

The viscosity of this concentrate solution is between about 30 and 190 pois, preferably between 50 and 140 pois, at 20°C. In order to stabilize the emulsion dispersing properties of the mixed concentrate solution, it is permissible to further admix dispersants, such as a nonionic surfactant, glycerine, or hexametaphosphoric acid salt, etc. The combined amount of this dispersant is between about 3 and 10% with respect to the amount of PTFE.

By combining the above concentrate solution with between 0.5% and 30%, preferably between 3 and 20%, of molybdenum disulfide having grain sizes of no more than 100 $\mu$ , preferably no more than 50 $\mu$ , the fiber dividing properties as well as strength, rigidity, and abrasion resistance can be improved.

The above concentrate solution is subjected to defoaming, and there is a problem at this time in that the moisture content becomes evaporated and causes the PTFE particles to aggregate. Since these aggregated particles can normally be 200 $\mu$  or greater, it is essential for the invention to prevent the formation of such aggregated particles. For this, the invention preferably employs a cryogenic (10°C or less) vacuum mixing method since it causes only a small amount of moisture to evaporate. The degree of vacuum is about 10 Torr. It is also preferable to filter the defoamed concentrate solution.

The above fiber-forming concentrate solution is then turned into fiber inside the aqueous solution of a solidifying bath composed of inorganic acid and/or inorganic acid salt. Sulfuric acid can be favorably

utilized as such inorganic acid, although nitric acid, hydrochloric acid, or phosphoric acid can be utilized instead. The content of the inorganic acid is between 0.1 and 50%, preferably between 0.5 and 35%, more preferably between 0.5 and 15%.

Moreover, sulfates such as antimony sulfate, zinc sulfate, and sodium sulfate can be mentioned as inorganic acid salt to be combined as necessary, although sodium sulfate is particularly preferred. This inorganic acid salt should be combined at about 30% or less.

The above-mentioned fiber-forming concentrate solution becomes extruded into the solidifying bath, in which it turns into multifilaments and becomes solidified. At this time, the fiber-forming rate should be slow at, for example, about between 20 and 50m per minute or less.

These solidified multifilaments are directly subjected to thorough refining in warm water of between 40 and 90°C, preferably around 80°C. Since this refining temperature is related to the generation of cavities, it should be controlled accurately. If producing fiber with irregular cross-sectional shapes, however, it is preferable to maintain the refining bath at a low temperature of no more than 60°C from the perspective of shape retention. Losing a sufficient amount of metal salt during this refining process will have a favorable effect in terms of fiber properties.

The refined filaments are then washed with alkali and squeezed.

As the alkali treatment bath, an aqueous solution of a compound selected from among the hydroxide, carbonate, or bicarbonate of an alkali metal or alkali earth metal is utilized. The concentration of the compound is between about 0.001 and 2% (between 0.0005 and 0.05 mol/l) with respect

to the fiber weight. Since such metal has the effect of promoting smooth calcination, it is attached to the fiber (between about 0.003 and 0.32%) in advance.

Directly after that, the alkali-treated bundle of multifilaments is subjected to calcination at between 300 and 450°C, preferably between 320 and 400°C. In this case, the calcination and drawing can be performed separately or simultaneously. The drawing should be at least 5 - 10 times. At this time, it should be selected that the calcination be carried out until the cellulose carbide becomes carbonized to 3.0% by weight or less. The obtained fiber is brown or black in color since it contains cellulose carbide.

The resultant PTFE fiber is whitened by being further oxidized and aged by means of air at no less than 300°C, preferably between 310 and 340°C, for at least 50 hours, preferably 60 hours or more.

Next, the invention will be explained in more detail based on an /103 embodiment.

#### [Embodiment of the Invention]

##### Embodiment 1

114 parts of an emulsion containing 60% of a PTFE resin dispersed in ion-exchanged water by using alkylaryl polyether alcohol as a dispersant was prepared and charged in a 8°C vacuum mixer with 100 parts of a viscose (cellulose 8.9%, caustic soda 5.4%, carbon disulfide 29%/cellulose quantity, ion-exchanged water for balance). The mixture was then blended and defoamed for 21 hours in a vacuum of 10 Torr to prepare a fiber-forming concentrate solution.

This fiber-forming concentrate solution was led to a spinneret having 240 0.12mm $\Phi$  holes at the rate of 43g per minute and was discharged into a solidifying bath, which was maintained at 23°C, at the rate of 23m per minute.

The resultant solidified fiber was led to a 80°C bath of ion-exchanged water, was thoroughly rinsed at the slow rate of about 29m per minute, and was squeezed with squeezing rollers. It was then immersed in an ion-exchanged solution in which the caustic soda concentration was 0.05 mol/l in order to impregnate the fiber with 0.32% by weight of caustic soda.

This alkali-containing fiber was calcined by being made to contact a roll having been heated to 380°C.

Then, this calcined fiber was drawn by 7 times while in contact with a 350°C heated roll.

In this relaxed state, the fiber was stored for 72 hours in a heated air atmosphere of 320°C.

The obtained PTFE fiber was white and had balanced properties of 1.3g/d strength, 16.1% elongation, and 12.3% dry-heat shrinking ratio (230°C  $\times$  30 minutes).

The small angle X-ray scattering intensity of the above fiber obtained at  $2\theta = 1^\circ$  by small angle X-ray scattering was 38cps, and the crystal size of the (110) crystal surface obtained by wide angle X-ray diffraction was 107Å.

In addition, marketed 6.7d white PTFE fiber had 1.3g/d strength, 40% elongation, and 5.3% dry-heat shrinking ratio (230°C  $\times$  30 minutes)

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and therefore was fiber with poor dimensional stability with an abnormally high elongation percentage.

The small angle X-ray scattering intensity of this fiber obtained at  $2\theta = 1^\circ$  by small angle X-ray scattering was 86cps, and the crystal size of the (110) crystal surface obtained by wide angle X-ray diffraction was 94Å.

#### [Effects of the Invention]

The present invention is ultrafine fiber and can be easily blended with and/or dispersed in various types of fiber or various types of resins. Therefore, it can be fully utilized in fields which were conventionally inapplicable.